HIGH TEMPERATURE OPTICAL PROPERTIES OF NANOPARTICLE SUSPENSIONS FOR DIRECT SOLAR ABSORPTION

Otanicar T.P.[1]*, DeJarnette D.[1], Mesgari S.[2], and Taylor R.A.[2]
*Author for correspondence
[1]Department of Mechanical Engineering,
The University of Tulsa,
Tulsa, OK, 74104
United States of America

[2]School of Mechanical and Manufacturing Engineering
University of South Wales,
Sydney, NSW, 2052
Australia

E-mail: todd-otanicar@utulsa.edu

ABSTRACT

Novel approaches for solar energy conversion are increasingly garnering research and commercial interest, particularly as hybrid thermal and electrical energy sources. Additionally, the need for systems capable of producing thermal energy at temperatures up to 300°C is growing as a means to provide process heat to industry and distributed generation for small communities. One such concept under rapid development since 2008 is the use of nanoparticles suspended in a heat transfer fluid that is directly exposed to incoming solar irradiance. Such collectors, often referred to as direct absorption solar collectors or volumetric solar collectors, have primarily been investigated (experimentally and numerically) at low temperatures due to the challenge of creating long-term stable suspensions at temperatures above 100°C. Working fluids with boiling points well above 100°C are not well investigated for nanoparticle dispersion. The likely reason for this gap is that many high temperature fluids are non-polar, which makes the stability problem even more challenging. Additionally, most surfactants work best in water and break down above 100ºC. Thus, even though many solar collectors operate above 100ºC and many applications require >100ºC heat, only a limited number of investigations have measured the optical properties of direct absorber liquids after exposure to these temperatures. To our knowledge no study has investigated nanofluid optical properties above 200°C. This represents critical missing data in the field, since high temperatures can affect particle stability, particle morphology, and plasmon resonance all which can lead to spectral changes in transmittance while changes in the fluid optical properties can occur at temperature. Additionally, the large coefficient of thermal expansion associated with common heat transfer fluids can result in significant changes to the working volume fraction leading to reduction in overall absorption magnitude. In this study, the optical properties of selected fluids in the solar spectrum were measured from room temperature up to 300°C. Glycol, silicon, hydrocarbon, diphenyl-oxide/biphenyl based fluids with nanotubes and indium tin oxide nanoparticles suspended with various surface treatments. As such, this paper provides a vital set of optical property data to enable further development of promising candidates for broadband spectrally selective nanofluid solar absorbers.

INTRODUCTION

Current solar energy systems account for 1% of electricity production in the U.S and ~7% in Germany. The majority of this is generated by PV systems which directly convert incoming photons to electricity. Concentrating solar thermal power (CSP) represents another method to generate electricity whereby solar energy is first converted to heat (steam) which can then be used to drive a turbine and generator. While PV can generate electricity at costs competitive with conventional sources, they are limited to daylight hours due to the cost of storage. CSP systems are more expensive than PV today, but their heat is easily stored and dispatched during peak times. Conventional CSP systems are almost exclusively based on surface absorption, where the surface is coated with a selective coating to ensure high levels of solar absorption while minimizing infrared emittance. Although these types of collectors represent the vast majority of both concentrating and non-concentrating based solar thermal energy production there exists an alternative approach, called volumetric or direct-absorption. These type of collectors typically have small particles suspended in the working fluid capable of directly absorbing the solar irradiance into the fluid. Within the recent literature these types of collectors have received increasing attention because of the ability to disperse nanoparticles with controlled optical properties into the heat transfer fluids. The earliest papers utilizing nanoparticles focused on modelling the system efficiency [1] and small scale experimental testing [2], all at temperatures below 100°C. Shortly thereafter experimental and numerical work for these systems under concentration was undertaken but limited to relatively low temperatures again [3]. Over the next few years multiple investigators have investigated the optical properties of a wide variety of nanoparticles for solar applications [4–8], analytical/numerical models [2,3,6,9–12], and experimental tests [2,3,7,13–15]. In addition to being used in conventional solar collectors, nanoparticles are receiving

significant new interest for applications in hybrid concentrating photovoltaic/thermal (CPV/T) applications because of the ability to design fluid filters that are spectrally selective [16–22].

While many of these studies have pushed the field forward, a significant limitation was the ability to create long-term stable solutions of nanoparticles at temperatures above 100°C, primarily due to limitations in surfactants. Since then significant progress has been made for creating stable suspensions at temperature. Using carbon nanotubes that are plasma treated Coulumbe et al. created stable particles demonstrated up to 170°C[23–25]. While these studies have demonstrated the potential for nanoparticle stability at high temperatures the optical property measurements are almost exclusively limited to temperatures near ambient. Such measurements are useful for establishing stability but don't provide important information about the optical properties at elevated temperatures at which the system will operate. Because of the limited data available at these temperatures we investigate here the optical properties of nanoparticle suspensions at temperatures up to 300 °C for a variety of heat transfer fluids and nanoparticles. Specifically we focus on broadband absorption using carbon nanotubes and selective infrared absorption using indium tin oxide (ITO) nanoparticles.

NOMENCLATURE

A	[-]	Absorbance
$MWCNT$	[-]	Multi-walled carbon nanotubes
T	[-]	Transmittance

Special characters
λ	[nm]	Wavelength

Subscripts
solar	Solar weighted

EXPERIMENTAL APPROACH

Spectra were taken at high temperature using a custom made heated transmission cell. The transmission cell has a 1 cm pathlength with sapphire windows. Fluid containing nanoparticles was inserted into the cell and both ends. One end was attached to an expansion tank to reduce pressure buildup in the optical chamber from thermal expansion of fluids at high temperature. Temperature was increased at a rate of one degree per minute to ensure stability of the transmission cell from thermal expansion. The heated transmission cell was placed directly in a UV-Vis spectrometer (Shimadzu 2600) for wavelengths between 300 and 1100 nm. For IR measurements, the heated flow cell was placed in an FTIR (Perkin Elmer Spectrum Two) for wavelengths from 1,000 to 4,000 nm. Spectra from the two systems were spliced together to form a single spectrum over the desired range of wavelengths. A general sketch of the apparatus is shown in Figure 1. Baseline of each spectra was the suspending fluid taken at temperature in the absence of nanoparticles. Fluids chosen for investigation here are: Duratherm S (boiling point 315°C at 1 ATM, silicone based), Therminol VP-1 (boiling point at 257°C 1 ATM, biphenyl/diphenyl oxide based), Dynalene MT (boiling point at 330°C 1 ATM, hydrocarbon based), and ethylene glycol (boiling point at 197°C 1 ATM). These fluids were chosen because of

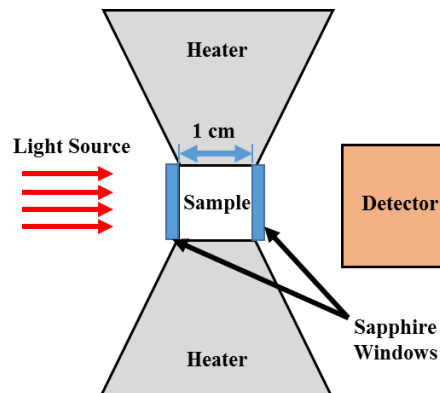their optical properties as well as ability to survive at high temperatures.

Figure 1 High temperature transmission cell for optical property determination

Nanoparticles selected were chosen because of their absorption across the full solar spectrum at relatively low cost. Specifically, we focus on single wall carbon nanotubes. The carbon nanotubes were purchased from Sigma-Aldrich and no additional process was performed than what is outlined below. The procedures used for ITO nanoparticles are outlined more below.

Chemical functionalization by KPS

For KPS functionalization method, 0.45 g of potassium persulfate (KPS) was mixed with 40 mg of MWCNTs dispersed in 50 ml of deionized water for 3h with a magnetic stirrer at 85°C and the pH of the reaction system was adjusted to 13 by adding concentrated potassium hydroxide (KOH) solution. After cooling down to room temperature, the solution was diluted with water and centrifuged at 3000 rpm for 20 min. The supernatant solution was then collected and filtered and washed with water to neutrality. The solids were then dried at 80°C overnight.

Chemical functionalization by UV-ozone

For the UVO functionalization method, 100 mg of MWCNTs (purchased from Sigma) was treated using a UV-ozone generator (PSD-UV8, Novascan Technologies) for 60min. MWCNTs were stirred at 10 min intervals to ensure a relatively uniform UVO exposure.

Plasma functionalization

For the plasma functionalization method, MWCNTs grown directly on a stainless steel mesh by thermal chemical vapor deposition, were treated with argon/oxygen/ethane plasma (radio frequency of 13.56 MHz) for 20 min. The plasma functionalised MWCNTs were then separated from the stainless steel mesh using bath sonication.

Preparation of CNT Suspensions

The functionalised MWCNTs were dispersed in the base fluids (Dynalene, Therminol, Duratherm, Glycol) by probe sonication at 20 W in a water-ice bath for 20 mins. The desired weight fraction of the samples was 33 mg/L to achieve a

measurable transmission/absorption signal in the spectrophotometers used.

Synthesis and Suspension of ITO Nanocrystals

Indium tin oxide nanoparticles were synthesized using the procedures reported by Garcia et al.[26]. The as synthesized ITO nanoparticles were not soluble in Duratherm. Therefore, in order to solubilize the ITO particles in Duratherm, one will need to replace the OLAM with a Duratherm compatible ligand, in this case (6-7% AMINOPROPYLMETHYLSILOXANE) DIMETHYLSILOXANE COPOLYMER, 80-120 cSt, a PDMS-type ligand, through refluxing.

RESULTS

Because of the nature of attempting to work with multiple different types of fluids and stabilization procedures not all combinations of fluid and surface treatment/functionalization results in stable nanoparticle solutions. Outlined in Table 1 is the results of the initial attempts to suspend the carbon nanotubes in different working fluids that then sat undisturbed for 24 hours.

Table 1 24-hour stability of carbon nanotubes with different surface treatments in different heat transfer fluids

Fluid/Surface Functionalization	Plasma	UVO	KPS
Duratherm S	Stable	Rapid Fall Out	Did not mix
Dynalene MT	Fall out	Stable	Did not mix
Therminol VP-1	Stable	Did not mix	Did not mix
Glycol	Stable	Stable	Stable

As will be shown later some of these particles remain stable while others remain stable only up to certain temperature limits. Representative samples of the 3 categories (stable, fall out and did not mix) outlined in Table 1 are shown in Figure 2.
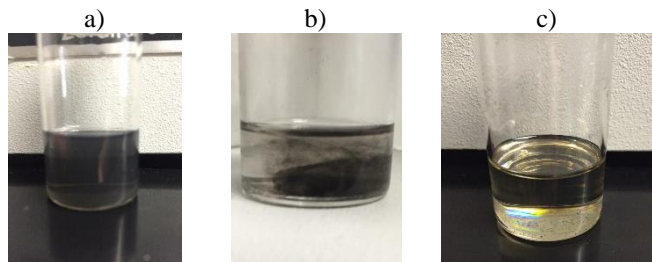

Figure 2 Pictures of Carbon Nanotubes in Duratherm with: a) plasma treatment, b) UVO treatment, and c) KPS treatment

From these images it can be seen that the plasma treated sample creates a uniform distribution with no visible aggregates,

while the UVO solution will initially disperses quickly forms agglomerates that fall out of solution. The KPS sample always remained as small particles in the bottom of the jar even after vigorous sonication efforts.

Temperature Dependent Transmission

Once the solutions were prepared the samples were tested in the experimental setup to observe the transmission as a function of temperature. The temperature response of the pure fluids can be seen in Figure 3.
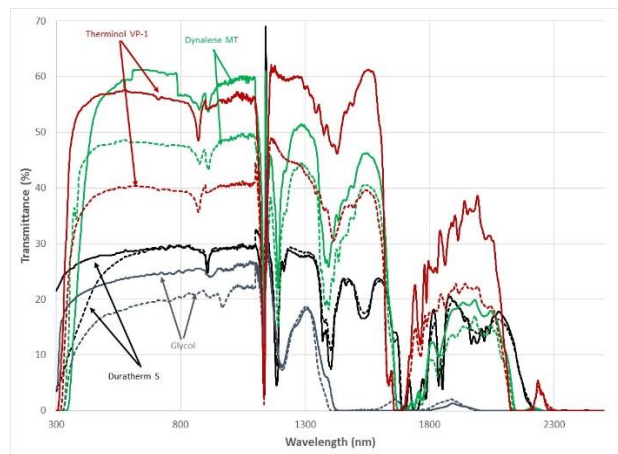

Figure 3 Transmittance as function of temperature. Solid lines at 25°C dashed lines at 300°C (Duratherm S and Dynalene MT), 250°C (Therminol VP-1) and 195°C (Glycol)

First, it should be noted the variation in the absolute level of transmission is a result of the experimental setup. As the setup is a non-standard modification to a conventional spectrophotometer the alignment is not as accurate as conventional setup. The large differences seen in absolute transmittance between two fluids is a reflection of this as all of the fluids are highly transparent as shown in previous work[27]. For each sample we try to obtain the best alignment possible but in some cases this results in lower values, additionally the window is smaller than a typical spectrometer window resulting in some blocking. Further the windows are sapphire with a higher refractive index than typical quartz cuvettes. With that in mind the relative trends are all valid as once the system is installed it is not adjusted throughout the experiment. As seen the used of Dynalene MT, Therminol VP-1 and glycol all result in a decrease in transmittance at increased temperatures. This can be attributed to two things. First, the refractive index of the base fluid typically decreases with temperature resulting in a higher Fresnel reflection from the interface of the fluid and the window. Second, a slight browning was observed in the Dynalene and Therminol as high temperatures were obtained. While not problematic for volumetric collectors absorbing the whole spectrum, this would pose a problem for CPV/T collectors. Plots are made till 2400 nm as afterwards all fluids absorb the incoming light completely. The noise seen near 1000 nm is from the FTIR equipment itself.

Representative results are shown for one of the stable fluids in Figure 4 and one solution where significant particle precipitation was observed at temperature in Figure 5.
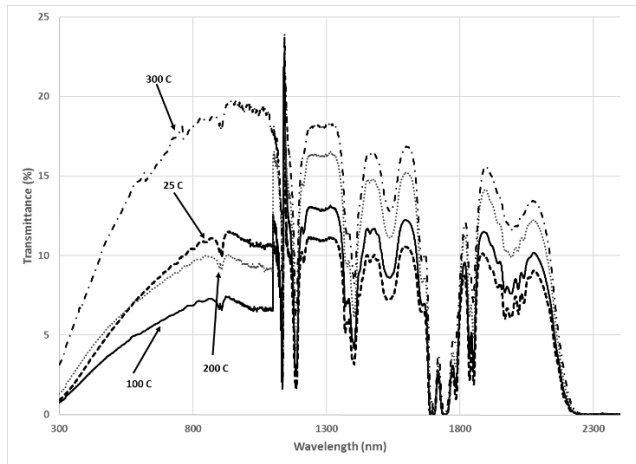

Figure 4 Transmittance of Duratherm S with plasma treated carbon nanotubes at temperatures from 25-300°C

As seen in Figure 4 multiple competing effects can be observed. First, at wavelengths from the UV-Visible the transmission is at first decreasing, a result of the basefluid until a large increase is observed. This final increase is a result from the expansion of the fluid, which all have significant coefficients of thermal expansion. This results in an effective decrease in volume fraction and consequent increase in transmittance. This is also observed in the infrared, where the base fluid is primarily independent of temperature, but the transmittance continually increases.

Figure 5 is the result for plasma coated particles in ethylene glycol. In this case the transmittance increases the entire time but this is contrary to the results of Figure 3 due to particle agglomeration and fall out. Although we would expect an increase in transmittance from fluid expansion, visual inspection demonstrated serious particle agglomeration as temperatures increase over 100°C. Similar results were observed for plasma treated particles in Dynalene and Therminol, and UVO treated particles in Dynalene and Therminol.
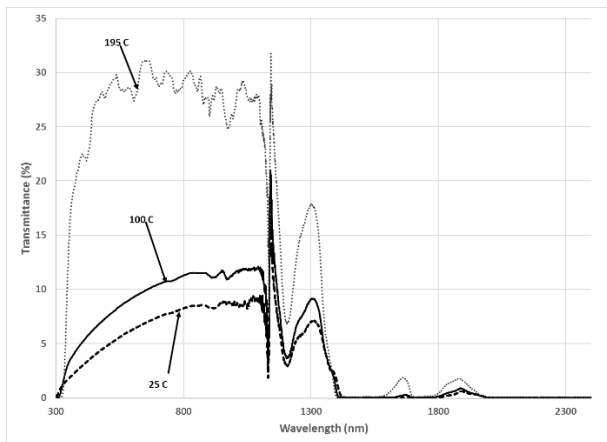

Figure 5 Transmittance of Ethylene Glycol with plasma treated carbon nanotubes at temperatures from 25-195°C

Significantly different behaviour was observed for the ITO particle compared to the nanotubes, for instance the primary absorption is in the infrared[26], because of this we only focus on the region of primary absorption. Results of spectral measurements are given in Figure 6. Measured spectra can be considered in three separate regions. From 25 to 150 °C, spectra remained relatively constant. After this point, the spectra began to blueshift and increase in amplitude at the intermediate temperature of 200°C. Finally, spectra taken at 250, 275, and 300 °C were all relatively constant as the temperature dynamics balanced out. In total, it was observed that a blue shift of the peak location from 2105 to 1740 and increase in the spectral amplitude of 158% occurred from ambient to 300 °C. It is suspected that high temperature caused rearrangement of tin atoms to be localized around the exterior of the nanocrystal[28]. Since plasmon resonance of ITO is caused by excess carriers from the tin concentration, the rearrangement causes a diffusion of tin into the ITO lattice giving a more well-blended atomic mixture.
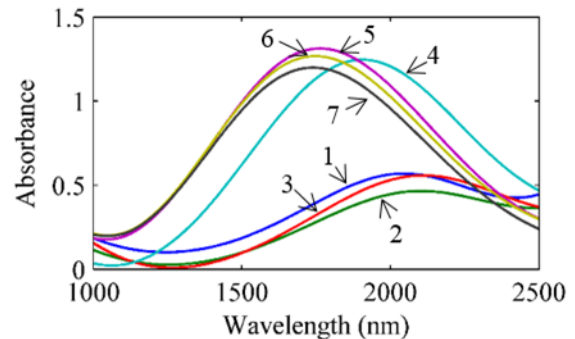

Figure 6 Variation of spectral absorbance as a function of temperature for ITO nanoparticles in Duratherm S (1 corresponds to 25°C with subsequent numbers in increments of 25°C)

While Figure 6 gives some insight into the change in optical properties, it is possible to quantify the shifting of the plasmon peak as a function of wavelength. This effect is indicated in Figure 7.
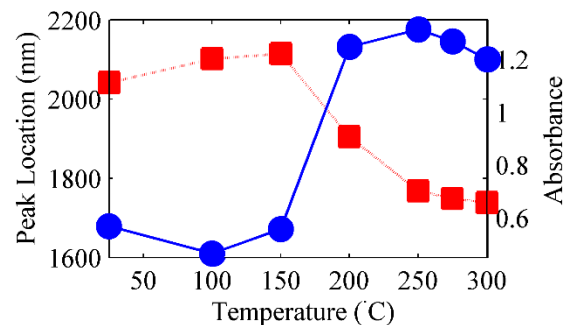
Figure 7 Trends in peak location (red-squares) and absorbance amplitude (blue-circles) for ITO nanocrystals as a function of temperature

As shown in Figure 7 the blueshift in plasmon resonance occurs at roughly 150°C with a blueshift of approximately 400 nm.

Solar Weighted Absorbance

While measuring the temperature dependent transmittance/absorbance provides useful information an important metric for judging the effectiveness of any absorber system in solar energy is the solar weighted absorbance, as defined below[29]. We only use this metric for the carbon nanotubes that are achieving bulk absorption as the metric is not as useful for a selective particle like ITO.

$$A_{solar} = \frac{\int E_\lambda (1-T)d\lambda}{\int E_\lambda d\lambda} \qquad (1)$$

where E_λ is the incident spectral solar flux on the system, and T is the transmittance. Although this approximation counts the reflection in the absorption it still provides a reasonable estimate. Here we focus on the change in solar weighted absorbance as we go too higher temperatures. The spectral solar flux is approximated by a blackbody with a temperature of 5800 K here[30]. The results are shown in Table 2 for the most promising fluid candidates.

Table 2 Solar Weighted Absorbance of carbon nanotube suspensions between room temperature and max operational temperature at 101 kPa.

Fluid	Treatment	Change in A_{solar}
Duratherm S	Plasma	-5.7%
	UVO	-5.9%
Glycol	UVO	-7.2%
	KPS	-2.5%

CONCLUSION

Demonstrated above are some of the first measurements of the optical properties of nanoparticle suspensions at high temperatures. Specifically, it was observed that through appropriate synthesis and surface treatment procedures stable particle suspensions can be achieved. For carbon nanotubes in various heat transfer liquids an overall increase in transmittance is observed due to the decrease in volume fraction caused by the significant thermal expansion of the fluid. This effect, combined with the impact of changes in the base fluid refractive index, results in an overall decrease in the solar weighted absorbance of 2.5-7%. While carbon nanotubes are broadband absorbers, ITO nanocrystals are spectrally selective infrared absorbers with tunable resonance depending on tin doping. Under heating the

plasmon resonance shifts due to suspected changes in the tin dopant distribution within the particle. Overall these results show promise for using nanoparticle suspensions in direct absorption solar thermal systems as the particles can be made stable and only minor changes in absorption are observed. This is important for further development of nanoparticle based direct absorption solar collectors. To date, most of the work in this area has been limited to low temperature applications (<100°C) but these results demonstrate that both broadband solar absorbing particles and spectrally selective particles can be made and stabilized. Importantly these results have been measured at elevated temperatures at which they will be operating while deployed in a solar collector, the first to our knowledge at these temperatures. These results also show that care should be taken to consider the optical properties at temperature as they will be different than those of room temperature.

REFERENCES

[1] Tyagi, H., Phelan, P., and Prasher, R., 2009, "Predicted efficiency of a low-temperature nanofluid-based direct absorption solar collector," J. Sol. Energy Eng., **131**(4), p. 041004.

[2] Otanicar, T. P., Phelan, P. E., Prasher, R. S., Rosengarten, G., and Taylor, R. a., 2010, "Nanofluid-based direct absorption solar collector," J. Renew. Sustain. Energy, **2**(3), p. 033102.

[3] Taylor, R. A., Phelan, P. E., Otanicar, T. P., Walker, C. a., Nguyen, M., Trimble, S., and Prasher, R., 2011, "Applicability of nanofluids in high flux solar collectors," J. Renew. Sustain. Energy, **3**(2), p. 023104.

[4] Mercatelli, L., Sani, E., Zaccanti, G., Martelli, F., Di Ninni, P., Barison, S., Pagura, C., Agresti, F., and Jafrancesco, D., 2011, "Absorption and scattering properties of carbon nanohorn-based nanofluids for direct sunlight absorbers.," Nanoscale Res. Lett., **6**(1), p. 282.

[5] Taylor, R. A., Phelan, P. E., Otanicar, T. P., Adrian, R., and Prasher, R., 2011, "Nanofluid optical property characterization: towards efficient direct absorption solar collectors.," Nanoscale Res. Lett., **6**(1), p. 225.

[6] Hewakuruppu, Y. L., Taylor, R. a., Tyagi, H., Khullar, V., Otanicar, T., Coulombe, S., and Hordy, N., 2015, "Limits of selectivity of direct volumetric solar absorption," Sol. Energy, **114**, pp. 206–216.

[7] Taylor, R., Coulombe, S., Otanicar, T., Phelan, P., Gunawan, A., Lv, W., Rosengarten, G., Prasher, R., and Tyagi, H., 2013, "Small particles, big impacts: A review of the diverse applications of nanofluids," J. Appl. Phys., **113**(011301).

[8]   Zhu, Q., Cui, Y., Mu, L., and Tang, L., 2012, "Characterization of Thermal Radiative Properties of Nanofluids for Selective Absorption of Solar Radiation," Int. J. Thermophys., **34**(12), pp. 2307–2321.

[9]   Khullar, V., Tyagi, H., Phelan, P. E., Otanicar, T. P., Singh, H., and Taylor, R. a., 2013, "Solar Energy Harvesting Using Nanofluids-Based Concentrating Solar Collector," J. Nanotechnol. Eng. Med., **3**(3), p. 031003.

[10]   Lee, B. J., Park, K., Walsh, T., and Xu, L., 2012, "Radiative Heat Transfer Analysis in Plasmonic Nanofluids for Direct Solar Thermal Absorption," J. Sol. Energy Eng., **134**(2), p. 021009.

[11]   Khullar, V., Tyagi, H., Hordy, N., Otanicar, T. P., Hewakuruppu, Y., Modi, P., and Taylor, R. a., 2014, "Harvesting solar thermal energy through nanofluid-based volumetric absorption systems," Int. J. Heat Mass Transf., **77**, pp. 377–384.

[12]   Otanicar, T. P., Phelan, P. E., Taylor, R. a., and Tyagi, H., 2011, "Spatially Varying Extinction Coefficient for Direct Absorption Solar Thermal Collector Optimization," J. Sol. Energy Eng., **133**(2), p. 024501.

[13]   Taylor, R. A., Phelan, P. E., Otanicar, T., Adrian, R. J., and Prasher, R. S., 2009, "Vapor generation in a nanoparticle liquid suspension using a focused, continuous laser," Appl. Phys. Lett., **95**(16), p. 161907.

[14]   Neumann, O., Urban, A., Day, J., Lal, S., Nordlander, P., and Halas, N. J., 2012, "Solar Vapor Generation Enabled by Nanoparticles.," ACS Nano.

[15]   Lenert, A., and Wang, E. N., 2012, "Optimization of nanofluid volumetric receivers for solar thermal energy conversion," Sol. Energy, **86**, pp. 253–265.

[16]   DeJarnette, D., Otanicar, T., Brekke, N., Hari, P., Roberts, K., Saunders, A. E., and Morad, R., 2014, "Plasmonic nanoparticle based spectral fluid filters for concentrating PV/T collectors," SPIE Sol. Energy+ Technol., pp. 917509–917509–13.

[17]   DeJarnette, D., Otanicar, T., Brekke, N., Hari, P., and Roberts, K., 2015, "Selective spectral filtration with nanoparticles for concentrating solar collectors," J. Photonics Energy, **5**(1), p. 057008.

[18]   Jing, D., Hu, Y., Liu, M., Wei, J., and Guo, L., 2015, "Preparation of highly dispersed nanofluid and CFD study of its utilization in a concentrating PV/T system," Sol. Energy, **112**, pp. 30–40.

[19]   Otanicar, T. P., Taylor, R. A., and Telang, C., 2013, "Photovoltaic/thermal system performance utilizing thin film and nanoparticle dispersion based optical filters," J. Renew. Sustain. Energy, **5**(3), p. 033124.

[20]   Saroha, S., Mittal, T., Modi, P. J., Bhalla, V., Khullar, V., Tyagi, H., Taylor, R. a., and Otanicar, T. P., 2015, "Theoretical Analysis and Testing of Nanofluids-Based Solar Photovoltaic/Thermal Hybrid Collector," J. Heat Transfer, **137**(9), p. 091015.

[21]   Taylor, R. A., Otanicar, T. P., and Rosengarten, G., 2012, "Nanofluid-Based Optical Filter Optimization for PV/T Systems," Nat. Light Sci. Appl., **1**.

[22]   Brekke, N., Otanicar, T., DeJarnette, D., and Harikumar, P., 2016, "A Parametric Investigation of a Concentrating PV/T System with Spectral Filtering Utilizing a 2-D Heat Transfer Model," J. Sol. Energy Eng.

[23]   Tavares, J., and Coulombe, S., 2011, "Dual plasma synthesis and characterization of a stable copper–ethylene glycol nanofluid," Powder Technol., **210**(2), pp. 132–142.

[24]   Hordy, N., Rabilloud, D., Meunier, J.-L., and Coulombe, S., 2014, "High temperature and long-term stability of carbon nanotube nanofluids for direct absorption solar thermal collectors," Sol. Energy, **105**, pp. 82–90.

[25]   Mesgari, S., Coulombe, S., Hordy, N., and Taylor, R. A., 2015, "Thermal stability of carbon nanotube-based nanofluids for solar thermal collectors," Mater. Res. Innov., **19**(S5), pp. S5–650–S5–653.

[26]   Garcia, G., Buonsanti, R., Runnerstrom, E. L., Mendelsberg, R. J., Llordes, A., Anders, A., Richardson, T. J., and Milliron, D. J., 2011, "Dynamically modulating the surface plasmon resonance of doped semiconductor nanocrystals.," Nano Lett.

[27]   Looser, R., Vivar, M., and Everett, V., 2014, "Spectral characterisation and long-term performance analysis of various commercial Heat Transfer Fluids (HTF) as Direct-Absorption Filters for CPV-T beam-splitting applications," Appl. Energy, **113**, pp. 1496–1511.

[28]   Lounis, S. D., Runnerstrom, E. L., Bergerud, A., Nordlund, D., and Milliron, D. J., 2014, "Influence of Dopant Distribution on the Plasmonic Properties of Indium Tin Oxide Nanocrystals," J. Am. Chem. Soc., **136**(19), pp. 7110–7116.

[29]   Otanicar, T. P., Phelan, P. E., and Golden, J. S., 2009, "Optical properties of liquids for direct absorption solar thermal energy systems," Sol. Energy, **83**(7), pp. 969–977.

[30]   Duffie, J. A., and Beckman, W. A., 2006, Solar Engineering of Thermal Processes, Wiley.